Journal of Thermal Analysis and Calorimetry, Vol. 74 (2003) 697–708

THE SELF-COOLING EFFECT IN THE PROCESS OF DEHYDRATION OF $Li_2SO_4{\cdot}H_2O$, $CaSO_4{\cdot}2H_2O$ AND $CuSO_4{\cdot}5H_2O$ IN VACUUM

B. V. L'vov[1]* *and V. L. Ugolkov*[2]

[1]Department of Analytical Chemistry, St. Petersburg State Polytechnic University,
St. Petersburg 195251, Russia
[2]Laboratory of Thermodynamics and Kinetics, Institute of Silicate Chemistry,
St. Petersburg 199155, Russia

(Received May 27, 2003; in revised form August 11, 2003)

Abstract

The third-law method has been applied to the results of kinetic studies reported in the literature and obtained in this work to determine the *E* parameters of the Arrhenius equation and investigate the impact of self-cooling on the dehydration kinetics of $Li_2SO_4{\cdot}H_2O$, $CaSO_4{\cdot}2H_2O$ and $CuSO_4{\cdot}5H_2O$. The values obtained (104, 98 and 88 kJ mol^{-1}, respectively) are about 20% higher compared to the literature data calculated by the Arrhenius-plots method. This discrepancy is connected with the severe effect of self-cooling, which can reach several ten degrees at maximum temperatures of experiments.

Keywords: Arrhenius-plots method, dehydration, kinetics, physical approach, second-law method, self-cooling, third-law method

Introduction

The significance of the self-cooling effect in the process of endothermic decomposition reactions has been discussed in many books and reviews on thermal analysis (e.g., [1, 2]) and atomic absorption spectrometry [3]. Cooper and Garner [4] and Anous *et al*. [5] measured the real temperature of the chrome alum crystals with the use of a thermocouple junction inserted between two cemented together large crystals. Bertrand *et al*. [6] basing on the studies of the evaporation kinetics of a liquid (water, ethanol) and decompositions of several solid hydrates came to conclusion 'that phenomena such as the Topley–Smith effect, which has been classified as anomalous, are nothing more than the result of incorrectly assuming thermal equilibrium during the course of the reaction in heterogeneous systems'. However, only a few studies [4, 5, 7] performed in the period of 1930–1950 are known which take into account this effect in measurements of the dehydration rates and the corresponding Arrhenius parameters (*E* and *A*). All other workers assume (in many

---

* Author for correspondence: E-mail: borislvov@rambler.ru

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

cases, tacitly) that the value of self-cooling is negligible and might been ignored in such measurements.

In 1998, L'vov *et al*. published a series of papers [8–10] devoted to the quantitative modeling of temperature distribution in these heterogeneous systems and evaluation of the effect of self-cooling on the decomposition parameters of $Mg(OH)_2$ and $Li_2SO_4{\cdot}H_2O$. It was shown that the temperature difference between the temperature controlled heater and the sample (even for a single crystal) can reach under typical experimental conditions several ten degrees and introduce serious errors in the determination of kinetic parameters. Despite this justified conclusion, the situation has not been improved. In a recent paper by Modestov *et al*. [11] devoted to the dehydration kinetics of $Li_2SO_4{\cdot}H_2O$, the authors ignored these precautions.

The purpose of this work is to discuss more thoroughly the impact of the self-cooling effect on the results reported in [11] and earlier studies performed in the same laboratory of the Institute of Solid State Chemistry in Novosibirsk on the dehydration kinetics of $Li_2SO_4{\cdot}H_2O$ [12, 13], $CaSO_4{\cdot}2H_2O$ [14] and $CuSO_4{\cdot}5H_2O$ [15]. It should be noted that the experimental results in these works have been obtained with the use of unique and very sensitive apparatus and under clearly defined (and described) experimental conditions. This significantly facilitates the further analysis of the kinetic data reported in [11–15]. Unfortunately, many other publications on the decomposition of these reactants ([9] for a full list of papers on $Li_2SO_4{\cdot}H_2O$ dehydration) do not contain the necessary information. In addition to the analysis of the results reported in the literature, some experiments on the decomposition of $Li_2SO_4{\cdot}H_2O$ have been performed in this work.

The physical approach based on a scheme involving dissociative evaporation of the reactant with simultaneous condensation of the low-volatile product will be used below for the quantitative evaluation of kinetics. This approach advanced by Hertz and Langmuir and developed by L'vov has been successively employed in the interpretation of the mechanism and kinetics of thermal decomposition of metal oxides, nitrates, carbonates, azides, oxalates, hydrates and a number of other inorganic compounds [16–19]. The mechanism of congruent evaporation of hydrates is supported by the direct QMS observation of $Cu(NO_3)_2$ molecules in the gas phase at 100–170°C in the process of vacuum dehydration of $Cu(NO_3)_2{\cdot}3H_2O$ [20].

Theoretical

Methods for the determination of the E parameters

Three different methods can be used for the experimental determination of the E parameter: the Arrhenius-plots, the second-law and the third-law methods. The Arrhenius-plots method is based on a traditional form of the Arrhenius equation for the rate constant, k:

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{1}$$

A set of rate constants (k_1, k_2, k_3…) at a series of temperatures (T_1, T_2, T_3…) are plotted in ln$k$ *vs.* T^{-1} scale and a linear regression yields values for the slope (E/R) and the intercept (ln$A$).

The second-law and third-law methods are based on the application of the basic equation of chemical thermodynamics (the equilibrium character of decomposition reactions has received recently [17] a strong experimental confirmation)

$$\ln K_\mathrm{P} = \frac{\Delta_\mathrm{r} S_\mathrm{T}^0}{R} - \frac{\Delta_\mathrm{r} H_\mathrm{T}^0}{RT} \tag{2}$$

where $\Delta_\mathrm{r} S_\mathrm{T}^0$ and $\Delta_\mathrm{r} H_\mathrm{T}^0$ are the entropy and enthalpy changes and K_P is the equilibrium constant

$$K_\mathrm{P} = P_\mathrm{A} P_\mathrm{B}^\mathrm{b} \tag{3}$$

for the decomposition (dehydration) reaction

$$\mathrm{A}b\mathrm{B}(s) \rightarrow \mathrm{A}(g) + b\mathrm{B}(g) \tag{4}$$

If we take into account that under congruent vaporization of the reactant [19]

$$P_\mathrm{A} = \frac{1}{b}\left(\frac{M_\mathrm{A}}{M_\mathrm{B}}\right)^{1/2} P_\mathrm{B} \tag{5}$$

where M_A and M_B are the molar masses of the products, then

$$K_\mathrm{P} = \frac{1}{b}\left(\frac{M_\mathrm{A}}{M_\mathrm{B}}\right)^{1/2} P_\mathrm{B}^\nu = cP_\mathrm{eq}^\nu \tag{6}$$

where ν is the total number of moles of gaseous products, i.e.

$$\nu = 1 + b \tag{7}$$

$$c \equiv \frac{1}{b}\left(\frac{M_\mathrm{A}}{M_\mathrm{B}}\right)^{1/2} \tag{8}$$

and P_eq is the equivalent pressure of the gaseous product B related to the rate of decomposition, J (in kg m^{-2} s^{-1}), by the Hertz–Langmuir equation [19]

$$P_\mathrm{eq} = \frac{(2\pi M_\mathrm{B} RT)^{1/2} J}{\gamma b M_\mathrm{B}} \tag{9}$$

Here γ=101325 Pa atm^{-1} is the conversion factor from pascals to atmospheres used to calculate partial pressures in chemical thermodynamics.

Taking into account Eq. (6) and the relationship $\Delta_\mathrm{r} H_\mathrm{T}^0/\nu = E$, valid for the equimolar mode of decomposition [21], we can present Eq. (2) as follows

$$\ln P_{\mathrm{eq}} = \frac{\Delta_{\mathrm{r}} S_{\mathrm{T}}^{0}}{\nu \mathrm{R}} - \frac{\ln c}{\nu} - \frac{E}{RT} \tag{10}$$

In case of the second-law method, a set of equivalent pressures (P_1, P_2, P_3…) at a series of temperatures (T_1, T_2, T_3…) are plotted in $\ln P_{\mathrm{eq}}$ *vs*. T^{-1} scale and a linear regression yields values for the slope (E/R) and the intercept ($\Delta_{\mathrm{r}} S_{\mathrm{T}}^{0}/\nu R - \ln c/\nu$). As can be seen from Eq. (9), $P_{\mathrm{eq}} \propto T^{0.5} J$. The additional dependence of P_{eq} on temperature causes a small increase in the slope of the $\ln P_{\mathrm{eq}}$ *vs*. T^{-1} plot compared to that for the Arrhenius $\ln k$ *vs*. T^{-1} plot. The resultant difference between the E parameters, calculated by the second-law and Arrhenius-plots methods, is equal to

$$\Delta E = \frac{R \ln(T_{\max}/T_{\min})}{2(T_{\min}^{-1} - T_{\max}^{-1})} \tag{11}$$

where $T_{\min}$ and $T_{\max}$ are the lower and higher points of the temperature interval used. In most cases, this difference ranges from 1 to 2 kJ mol^{-1}.

In case of the third-law method, the value of $\Delta_{\mathrm{r}} S_{\mathrm{T}}^{0}$ in Eq. (10) is calculated from the known thermodynamic functions (e.g., [22, 23]) of the reaction components (or estimated from a comparison with $\Delta_{\mathrm{r}} S_{\mathrm{T}}^{0}$ values for similar compounds [17]) and, then, the E parameter can be determined from only one measured value of P_{eq}. In this case, Eq. (10) can be rewritten as

$$E = T\left[\frac{\Delta_{\mathrm{r}} S_{\mathrm{T}}^{0}}{\nu} - \frac{R \ln c}{\nu} - R \ln P_{\mathrm{eq}}\right] \tag{12}$$

As can be seen from a consideration of Eq. (12), the self-cooling effect in case of the third-law method, in contrast to the second-law method, results in overestimation of the calculated results.

Our analysis of the results for several tens of substances reported in [23], has shown that the data calculated by the third-law method are in general the order of magnitude more precise than those calculated by the second-law method. This has been supported recently by the results of application of the second-law and third-law methods to the determination of the E parameter for 20 different decomposition reactions [17–19].

Thermodynamic functions

To apply the third-law method for the calculation of the E parameters, it is necessary to know the entropy changes for the corresponding dehydration reactions and, therefore, the entropy values for all species (reactants and gaseous products) of these reactions. These values at 298 K are reported [22, 23] for all species considered in the present reactions except for gaseous molecules of $\mathrm{Li_2SO_4}$, $\mathrm{CaSO_4}$ and $\mathrm{CuSO_4}$. However, the entropy values for gaseous sulfates of some alkali metals are known. In Table 1, we collected these values for Na-, K-, Rb- and Cs-sulfates and corresponding gaseous oxides. As can be seen, the mean difference between the entropy values of these molecules (sulfate and oxide) is equal to 76.7±5.2 J mol^{-1} K^{-1}. If we assume that the same difference is valid for combination of sulfate and oxide molecules of Li, Ca and Cu, then it is possible to estimate the unknown entropy values (in J mol^{-1} K^{-1}) from the relationship:

$$S^0_{298}(\text{sulfate})=S^0_{298}(\text{oxide})+76.7 \tag{13}$$

The entropy values of Li_2O, CaO and CuO [22, 23] at 298 K in these calculations were taken to be 232.9, 219.6 and 234.7 J mol^{-1} K^{-1}. The entropy values for all components of dehydration reactions are presented in Table 2. The resultant entropy changes, $\Delta_r S^0_{298}$, and the stoichiometry corrections, $R\ln c/\nu$, appeared in Eq. (12), are listed in Table 3.

Table 1 The entropy values of some gaseous sulfates and oxides [22, 23]

Metal	S^0_{298}/J mol^{-1} K^{-1}		ΔS^0_{298}/J mol^{-1} K^{-1}
	M_2SO_4 (*g*)	M_2O (*g*)	
Na	344.8	271.5	73.3
K	365.3	293.7	71.6
Rb	391.2	313.0	78.2
Cs	410.0	326.8	83.2
Mean			76.6±5.2 (S.D.)

Table 2 The entropy values for all species of dehydration reactions [22, 23]

Species	S^0_{298}/J mol^{-1} K^{-1}
$Li_2SO_4 \cdot H_2O$ (*s*)	146.4
Li_2SO_4 (*s*)	309.5[a]
$CaSO_4 \cdot 2H_2O$ (*s*)	194.1
$CaSO_4$ (*g*)	296.2[a]
$CuSO_4 \cdot 5H_2O$ (*s*)	300.4
$CuSO_4$ (*g*)	311.3[a]
H_2O (*g*)	188.7

[a] Estimated in this work (Table 1 and Eq. (13))

Table 3 Corrections for stoichiometry and the entropy changes for dehydration reactions

Hydrate	*b*	ν	M_A/ kg mol^{-1}	M_B/ kg mol^{-1}	*c*	($R\ln c/\nu$)/ J mol^{-1} K^{-1}	($\Delta_r S^0_{298}/\nu$)/ J mol^{-1} K^{-1}
$Li_2SO_4 \cdot H_2O$	1	2	0.110	0.018	2.470	3.76	175.9
$CaSO_4 \cdot 2H_2O$	2	3	0.136	0.018	1.370	0.872	159.8
$CuSO_4 \cdot 5H_2O$	5	6	0.160	0.018	0.596	–0.717	159.1

Evaluation of the self-cooling effect

The magnitude of the self-cooling can be easily estimated from Eq. (12) if we assume that the only reason of overestimation for the experimental E_{exp} value, calculated by the third-law method, is the effect of self-cooling. If we further assume that the E value at the lowest temperature is free from this effect (i.e., the temperature of the sample, T_{s}, is equal to the temperature of the heater, T_{h}) and corresponds to the true value of the E parameter, E_{true}, then it is possible to find the actual temperature of the sample, T_{s}, for any higher temperature of decomposition. This temperature is equal:

$$T_{\mathrm{s}} = T_{\mathrm{h}} \frac{E_{\mathrm{true}}}{E_{\mathrm{exp}}} \tag{14}$$

if we neglect a small systematic decrease of both $\Delta_{\mathrm{r}} S_{\mathrm{T}}^{0}$ and $\Delta_{\mathrm{r}} H_{\mathrm{T}}^{0}$ values with temperature.

Smith and Topley [7] attempted to evaluate the self-cooling of $CuSO_4 \cdot 5H_2O$ crystals from a comparison between the energy received by the sample from the heater and the energy consumed for the decomposition. At the steady-state rate of decomposition, these energies are equilibrated. If we exclude any other ways of sample heating except of radiation from the temperature controlled support (or thermostat), then

$$\varepsilon\sigma(T_{\mathrm{h}}^{4} - T_{\mathrm{s}}^{4}) = \frac{J\Delta_{\mathrm{r}} H_{\mathrm{T}}^{0}}{bM_{\mathrm{B}}} \tag{15}$$

Here ε and σ are the efficient value of the emittance factor and the Stefan–Boltzmann constant ($5.67 \cdot 10^{-8}$ J s^{-1} m^{-2} K^{-4}). Similar equations were used also in the calculations of the heats of decomposition of chrome alum [4, 5]. As noted above, the sample temperature, T_{s}, was measured in these works with a thermocouple.

Experimental

The experiments were carried out with a Netzsch STA 429 instrument on the TG and DSC measuring head. The actual measured quantities were the mass change of the sample per time unit, $\Delta m/\Delta t$, and the absolute crucible temperature. An open alumina crucible 5.7 mm inner diameter and 4.0 mm high was used as a sample container. The reacting material was high purity powder of $Li_2SO_4 \cdot H_2O$. A powder sample (40 mg) introduced into a crucible was leveled and pressed manually (about 1 kg mm^{-2}) into a flat pellet. The total (outer) surface area of pellet was calculated taking into account the crucible diameter and the width of pellet (estimated from the sample mass and the apparent density of powder measured separately).

In experiments on determination of the E parameter, the sample chamber was evacuated to a residual pressure about $8 \cdot 10^{-8}$ atm with the use of rotation and oil-diffusion pumps. All measurements have been conducted at continuous pumping under isothermal conditions. The heating rate of the sample from the room temperature to intermediate one (20 K lower than the desired temperature) was 10 K min^{-1} and from intermediate to the desired temperature was 2 K min^{-1}. At the beginning of each measuring cycle, the system was heated at the temperature chosen, usually during 10 min, to reach a constant rate of the decomposition. The changes of the mass and surface area of crystals and powders during this period were taken into account. A decrease of the surface area, as was checked experimentally for different α values, was proportional to $(1-\alpha)^{2/3}$ where α is the decomposition degree. This relationship can be interpreted as the combined effect of decreasing of the size (surface area) and number of particles participating in the process of dehydration. Temperature was measured with Pt-Pt10%Rh thermocouple placed with its junction immediately below the crucible. Temperature variations in the process of mass-change measurements (usually, during 20–30 min) did not exceed ±0.2 K. A single measurement of the decomposition rate took entirely about 2 h.

The absolute value of the decomposition rate was estimated using the method proposed in our previous work [19]. It consists in the evaluation of the absolute decomposition rate of a powder sample (reduced to the unit of the outer surface area of a pellet formed by the powder sample in a cylindrical crucible). The value received is lowered by the correction (empirical) factor and then used for the calculation of the *E* parameter by the third-law method. The value of this factor (2.8±0.4), as was shown in [19], does not depend on the temperature, residual pressure of gas in the reactor, grain size and mass of a powder sample.

Results and discussion

This work

Experimental conditions and the results of calculation of the *E* parameter for $Li_2SO_4 \cdot H_2O$ dehydration by the third-law method are presented in Table 4. The average value of the *E* parameter (105.2±0.3 kJ mol^{-1}) is somewhat higher than the theoretical value of the *E* parameter (97 kJ mol^{-1}) estimated in [9] on the basis of the enthalpy change for this reaction. The discrepancy results from the overestimation in [9] of the magnitude of τ parameter, which corresponds to the fraction of the condensation energy transferred to the reactant in the process of condensation of primary decomposition product (gaseous molecules of Li_2SO_4). The best agreement between the theoretical and experimental values of the *E* parameter is reached at $\tau=0.56$ (instead of 0.60 [9]). (The problem of the appropriate choice of the τ parameter and its a priori estimation for different decomposition reactions has been discussed recently in [24].) The value of the *E* parameter (112 kJ mol^{-1}) calculated in [17] by the third-law method on the basis of experimental results reported in [13] is slightly overestimated as can be seen from the comparative data presented in Table 5.

It should be mentioned that, in contrast to the Arrhenius-plots method, when a number of points used for plotting reached 37 [12], 14 [14] and 15 [15] in cases of $Li_2SO_4 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$ dehydration (Table 5), only one point (at the lowest temperature) was used for the determination of the *E* parameter by the third-law method.

Table 4 Experimental conditions and results of calculation of the *E* parameter for $Li_2SO_4 \cdot H_2O$ dehydration by the third-law method (this work)

Sample^a	T/K	m_0/mg	S_0/mm^2	α_m^{b}	S_m^{c}/mm^2	$(\Delta m/\Delta t)^d$/μg s^{-1}	J_{corr}^{e}/kg m^{-2} s^{-1}	P_{eq}/atm	E/kJ mol^{-1}
Powder	342.9	40	68.94	0.524	42.02	1.00	$8.50 \cdot 10^{-6}$	$8.37 \cdot 10^{-8}$	105.5
Powder	335.6	40	68.94	0.145	62.10	0.82	$4.72 \cdot 10^{-6}$	$4.60 \cdot 10^{-8}$	104.9

[a] The apparent density of pellets prepared from this powder is equal to 1567 kg m^{-3}

[b] The decomposition degree by the time of measurement

[c] The surface area by the time of measurement calculated by the equation $S_m = S_0(1-\alpha_m)^{2/3}$

[d] Measured in the interval from 80 to 100 min and from 70 to 90 min for the first and the second experiment

[e] $J_{corr} = (\Delta m/\Delta t)/(2.8S_m)$

Table 5 Experimental conditions and results of calculations of the *E* parameter for dehydration of $Li_2SO_4 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$ (the literature data)

Hydrate	Balance	Point number	ΔT/K	J/kg m^{-2} s^{-1}		P_{eq}/atm		E/kJ mol^{-1}		Ref.
				at T_{min}	at T_{max}	at T_{min}	at T_{max}	Reported	Third-law^a	
$Li_2SO_4 \cdot H_2O$	quartz crystal	37	**300**–400	$5.70 \cdot 10^{-8}$	$6.24 \cdot 10^{-4}$	**$8.66 \cdot 10^{-10}$**	$6.63 \cdot 10^{-6}$	87.1±0.8	**103.7**/108.5	[12]
	quartz crystal	6	315–363	$1.09 \cdot 10^{-7}$	$7.25 \cdot 10^{-6}$	$9.75 \cdot 10^{-10}$	$7.35 \cdot 10^{-8}$	84.9±0.8	108.6/112.1	[13]
	electronic	9	348–433	$2.73 \cdot 10^{-5}$	$1.12 \cdot 10^{-3}$	$2.60 \cdot 10^{-7}$	$1.24 \cdot 10^{-5}$	50.6	103.8/115.2	[11]
$CaSO_4 \cdot 2H_2O$	quartz crystal	14	**288**–357	$8.71 \cdot 10^{-8}$	$7.08 \cdot 10^{-5}$	**$3.93 \cdot 10^{-10}$**	$3.56 \cdot 10^{-7}$	82.8±1.6	**97.6**/100.8	[14]
$CuSO_4 \cdot 5H_2O$	quartz spring	8	273–316	$5.38 \cdot 10^{-7}$	$1.95 \cdot 10^{-5}$	$1.18 \cdot 10^{-9}$	$4.58 \cdot 10^{-8}$	76.2^b	90.3/94.9	[7]
	quartz crystal	15	**255**–303	$1.21 \cdot 10^{-7}$	$3.63 \cdot 10^{-5}$	**$2.42 \cdot 10^{-10}$**	$8.40 \cdot 10^{-8}$	74.5±0.8	**87.7**/89.5	[15]

[a] At T_{min} and T_{max}, respectively

[b] Corrected by the authors [7] for self-cooling

The literature data

The experimental conditions reported in [7, 11–15] and the results of our calculations of the *E* parameters by the third-law method for $Li_2SO_4 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$ dehydration are presented in Table 5. Single crystals of hydrates were used in all works. The size of samples varied over a wide range. The parallelepiped-like crystals (5×3×0.3 mm) were used in [12], disk-like crystals 6 mm in diameter and 1 mm thick in [13–15] and disk-like crystals 6 mm in diameter and 10 mm thick in [11]. To improve thermal contact between the sample and the thermostatically controlled support and prevent the reaction on the side surface, the bottom faces and the side surfaces of crystals were covered with an indium-gallium eutectic [11–15]. The single crystals of $CuSO_4 \cdot 5H_2O$ used by Smith and Topley [7] were about 50–60 mg in mass and 60–80 mm^2 in surface area.

The dehydration rate was measured under isothermal conditions by a quartz-crystal microbalance in [12–15], by a novel electronic balance (developed in the Novosibirsk Institute of Solid State Chemistry) in [11] and by a helical-silica-spring balance in [7]. The reaction chamber was continuously evacuated to maintain the residual pressure within $4 \cdot 10^{-5}$ Pa. The temperature control of the sample support [11–15] (or the thermostat [7]) was accurate to ±0.1°C.

As can be seen from Table 5, the *E* parameters calculated in this work by the third-law method in all cases are much higher than the *E* parameters calculated in corresponding works by the Arrhenius-plots method. (The error in the calculation of the *E* parameters related with the uncertainty in $\Delta_r S^0_{298}/\nu$ ratio is less then 1 kJ mol^{-1}.) The data obtained for the lowest temperatures in [12, 14, 15] (marked by bold) are taken as the most reliable. The equivalent pressure here was in the range $(2–9) \cdot 10^{-10}$ atm. However, even in these cases, the difference in the *E* parameters calculated by the third-law and Arrhenius-plots methods is equal to 19% for $Li_2SO_4 \cdot H_2O$ and 18% for $CaSO_4 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$. The maximum discrepancy (50.6 and 103.8 kJ mol^{-1}) is observed for the results obtained in a recent paper on $Li_2SO_4 \cdot H_2O$ dehydration [11].

As expected, the *E* parameters calculated by the third-law method at maximum temperatures of the experiments are somewhat higher than those at minimum temperatures. In cases of the most reliable works, the difference is about 5% [12], 3% [14] and 2% [15]. These values correlate in proportion to the temperature intervals, $T_{max}–T_{min}$, used in the experiments in the corresponding works: 100 K [12], 69 K [14] and 48 K [15].

The self-cooling effect

In the further evaluation of the self-cooling effect, we assumed that the *E* parameters calculated at minimum temperatures in [12, 14, 15] represent the true values of this parameter, E_{true}, in the absence of self-cooling. The values of self-cooling at higher temperatures of dehydration calculated by Eq. (14) are presented in Table 6. These values vary within a wide range: from a few degrees at moderate temperatures to several ten degrees at maximum temperatures, and are in agreement with the maximum values of self-cooling (ΔT=–12 K [4] and –9 K [5]) measured experimentally by direct methods for the dehydration of chrome alum at 308 K. The absolute rate of dehydration, *J*, for chrome alum was about $2\cdot 10^{-4}$ kg m^{-2} s^{-1}, what is comparable with the *J* values (at T_{max}) listed in Table 5. In particular, the *J* value for $Li_2SO_4\cdot H_2O$ at 443 K [11] is about 6 times higher.

Table 6 The self-cooling effect

Hydrate	Reference	T_{min}/K	ΔT/K	T_{max}/K	ΔT/K
$Li_2SO_4\cdot H_2O$	[12]	300	0.0	400	–17.7
	[13]	315	–14.2	363	–27.2
	[11]	348	–0.3	433	–43.2
	this work	343	–5.9	–	–
	this work	336	–3.8	–	–
$CaSO_4\cdot 2H_2O$	[14]	288	0.0	357	–11.3
$CuSO_4\cdot 5H_2O$	[7]	273	–7.9	316	–24.0
	[15]	255	0.0	303	–6.1

To check the validity of the self-cooling values found in this work, we re-calculated the *E* parameters by the second-law method basing on the values of P_{eq} listed in Table 5 at T_{min} and T_{max} and taking into account the corresponding temperature corrections in Table 6. These values together with the results obtained by other methods are presented in Table 7. As can be seen, these re-calculated values are in good agreement with the values of *E* parameter calculated by the third-law method (especially, with the 'true' values, E_{true}, used for the evaluation of the self-cooling). The difference between the *E* parameters calculated by the second-law and Arrhenius-plots methods without taking into account the self-cooling effect is in the range from 1.2 to 1.6 kJ mol^{-1}.

Table 7 The values of the *E* parameter (in kJ mol^{-1}) calculated by different methods

Hydrate	Arrhenius-plots (Reported)	Second-law		Third-law (at T_{min})
		Corrected[a]	Re-calculated[b]	
$Li_2SO_4\cdot H_2O$	87.1 [12]	88.5	103.6	103.7
	84.9 [13]	86.3	103.7	108.6
	50.6 [11]	52.2	103.4	103.8
	– [this work]	–	–	105.2
$CaSO_4\cdot 2H_2O$	82.8 [14]	84.1	97.7	97.6
$CuSO_4\cdot 5H_2O$	76.2[c] [7]	77.4	87.5	90.3
	74.5 [15]	75.7	87.9	87.7

[a] Corrected by Eq. (11) for the $T^{0.5}$ factor differing the second-law method from the Arrhenius-plots method

[b] The self-cooling is taken into account (Table 6)

[c] Corrected by the authors [7] for self-cooling

As noted above, some workers attempted to estimate the self-cooling effect [7] and the heat of dehydration [4, 5] on the base of Eq. (15), admitting the only source of sample heating via radiation from the heater. In these calculations, the authors [4, 5, 7] assumed the emittance factor, ε, to be equal to that for blackbody conditions, i.e., ε=1. The conclusions deduced from these calculations are wrong. It is easy to show that the power of radiation (W_r) from the temperature controlled support at low (room) temperatures is significantly smaller compared with the power (W_c) actually consumed by the reactant for the decomposition. Let us consider, as an example, the case of dehydration of $Li_2SO_4 \cdot H_2O$ at 400 K [12]. In this case, T_h=400 K and T_s=382.3 K (Table 5). Therefore, at the maximum value of the emittance factor (ε=1), $W_r=1\times5.67\cdot10^{-8}\times(400^4-382.3^4)=240$ J m^{-2} s^{-1}. The parameters determining the W_c value in Eq. (15) are the following: M_B=0.018 kg mol^{-1}, b=1, $J=6.24\cdot10^{-4}$ kg m^{-2} s^{-1} and $\Delta_r H_T^0=2E=2.074\cdot10^5$ J mol^{-1} (Tables 3 and 5). We obtain W_c=7190 J m^{-2} s^{-1}. As we see, the power consumed is 30 times higher compared to the radiation power. If we take into account that the efficient value of emittance factor at low temperature is actually close to 0.01 [18] then this difference should proportionally increase still further.

It means that the main source of sample heating in works considered in this paper (except of [7]) is thermal conduction through the bottom surface of the sample covered with an indium–gallium eutectic and contacted with the surface of the thermostatically controlled support. In cases of thin crystals [12, 14, 15], the efficiency of heating was apparently higher than in case of large crystals [11]. This difference in sampling as well as the higher dehydration temperatures used in [11] explain the high value of self-cooling ($\Delta T=-43$ at 433 K) and anomalously low value of the E parameter (50.6 kJ mol^{-1}) obtained by Modestov *et al*. [11] compared to 87.1 and 84.9 kJ mol^{-1} determined in the same laboratory earlier [12, 13].

The values of self-cooling effect and the E parameter calculated by Smith and Topley [9] at condition ε=1 were also underestimated. Compared to the ΔT values reported (–0.3 and –8.1 K at 273 and 316 K), they are equal to –7.9 and –24 K (Table 5). As a result, the correction of the E parameter for self-cooling in [7] was less than it should have been (Table 6).

Conclusions

The third-law method has been applied to the results of kinetic studies reported in the literature and obtained in this work to determine the values of the E parameters and investigate the impact of self-cooling on the dehydration kinetics of $Li_2SO_4 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$. The values obtained are about 20% higher compared to the literature data calculated by the Arrhenius-plots method. This discrepancy is connected with the severe effect of self-cooling which can reach several ten degrees at maximum temperatures of experiments. This conclusion is undoubtedly valid in relation to other reactants. After correction for the self-cooling, the results of calculation of the E parameters by the second-law method turned out to be in agreement with the values obtained by the third-law method.

This study demonstrated the advantages of the physical approach and the new methodology of kinetic investigations based on the third-law method over the usual approach in reliability of the obtained results, savings in time for experiments and in a unique possibility to evaluate the self-cooling effect.

References

1 W. E. Garner, Chemistry of the Solid State, Butterworths, London 1955.
2 A. K. Galwey and M. E. Brown, Thermal Decomposition of Ionic Solids, Elsevier, Amsterdam 1999.
3 B. V. L'vov, Atomic Absorption Spectrochemical Analysis, Adam Hilger, London 1970, p. 175.
4 M. M. Cooper and W. E. Garner, Proc. Roy. Soc. A, 174 (1940) 487.
5 M. M. Anous, R. S. Bradley and J. Colvin, J. Chem. Soc., (1951) 3348.
6 G. Bertrand, M. Lallemant, A. Mokhlisse and G. Watelle-Marion, J. Inorg. Nucl. Chem., 40 (1978) 819.
7 M. L. Smith and B. Topley, Proc. Roy. Soc. A, 134 (1931) 224.
8 B. V. L'vov, A. V. Novichikhin and A. O. Dyakov, Thermochim. Acta, 315 (1998) 135.
9 B. V. L'vov, Thermochim. Acta, 315 (1998) 145.
10 B. V. L'vov, A. V. Novichikhin and A. O. Dyakov, Thermochim. Acta, 315 (1998) 169.
11 A. N. Modestov, P. V. Poplaukhin and N. Z. Lyakhov, J. Therm. Anal. Cal., 65 (2001) 121.
12 V. B. Okhotnikov, B. I. Yakobson and N. Z. Lyakhov, React. Kinet. Catal. Lett., 23 (1983) 125.
13 N. A. Kirdyashkina and V. B. Okhotnikov, React. Kinet. Catal. Lett., 36 (1988) 417.
14 V. B. Okhotnikov, S. E. Petrov, B. I. Yakobson and N. Z. Lyakhov, Reactivity of Solids, 2 (1987) 359.
15 V. B. Okhotnikov and N. Z. Lyakhov, J. Solid State Chem., 53 (1984) 161.
16 B. V. L'vov, Thermochim. Acta, 373 (2001) 91.
17 B. V. L'vov, Thermochim. Acta, 389 (2002) 199.
18 B. V. L'vov, L. K. Polzik and V. L. Ugolkov, Thermochim. Acta, 390 (2002) 5.
19 B. V. L'vov and V. L. Ugolkov, Thermochim. Acta, 401 (2003) 139.
20 B. V. L'vov and A.V. Novichikhin, Spectrochim. Acta Part B, 50 (1995) 1459.
21 B. V. L'vov, Spectrochim. Acta Part B, 52 (1997) 1.
22 V. P. Glushko (Ed.), Thermodynamic Constants of Substances, Handbook in 10 volumes, Akad. Nauk SSSR, Moscow, 1965–1982 (in Russian).
23 V. P. Glushko (Ed.), Thermodynamic Properties of Individual Substances, Handbook in 4 volumes, Nauka, Moscow, 1978–1982 (in Russian).
24 B. V. L'vov and V. L. Ugolkov, Thermochim. Acta, in press.